



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US86/00376 <b>(22) International Filing Date:</b> 21 February 1986 (21.02.86) <b>(31) Priority Application Number:</b> 704,828 <b>(32) Priority Date:</b> 22 February 1985 (22.02.85) <b>(33) Priority Country:</b> US  <b>(71) Applicant:</b> A. E. STALEY MANUFACTURING COMPANY [US/US]; 2200 East Eldorado Street, Decatur, IL 62525 (US). <b>(72) Inventors:</b> ROTH, Claris, Deane ; 4159 Newcastle Drive, Decatur, IL 62526 (US). MOSER, Kenneth, B. ; 3054 MacArthur Road, Decatur, IL 62526 (US). <b>(74) Agents:</b> CAMPBELL, Michael, F.; A. E. Staley Manufacturing Company, 2200 East Eldorado Street, Decatur, IL 62525 (US) et al.		<b>(81) Designated States:</b> BE (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> DETERGENT COMPOSITION  <b>(57) Abstract</b>  Use of alkylene oxide adduction on a glycoside molecule to increase detergency.		

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DETERGENT COMPOSITIONBACKGROUND OF THE INVENTION

## 1. Field of the Invention.

5 This invention relates to materials which are useful as nonionic surfactants.

## 2. Description of the Art Practices.

Glycosides have long been known as materials which can function in detergent products. The glycosides are nonionic surfactants which are prepared through the reaction of a saccharide material and an alcohol. The alcohol portion of the molecule adds hydrophobic character whereas the saccharide portion of the molecule increases the water solubility. A measure of the degree of the water solubility can be obtained through a measurement known as the degree of polymerization of the glycoside. The degree of polymerization (or DP) is conveniently measured as the average number of saccharide molecules which have been joined together in forming the glycoside.

Mansfield et al in U. S. Patent 3,640,998 issued February 8, 1972 describes surfactants therein which have been reacted with ethylene oxide or propylene oxide. The apparent purpose in the Mansfield Patent for so treating the glycoside surfactant is to convert the residual fatty alcohol which was used in obtaining the glycoside to an alkoxylated alcohol. The alkoxylated alcohols are well known as nonionic surfactants. In the absence of treating the alcohol to form an alkoxylated alcohol, Mansfield was left with a large portion of unreacted fatty material in the reaction mixture as well as large amounts of lower (non-surfactant) glycosides. The presence of unreacted

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fatty material inhibits the cleaning ability of the composition. Additionally, the presence of lower glycosides  
5 diminishes the capacity of the composition to clean effectively.

The use of glycosides in detergent compositions is disclosed in U. S. Patent 4,483,779 issued November 20, 1984 to Llenado et al. The Llenado et al  
10 patent shows an unmodified glycoside surfactant in combination with other nonionic detergents including ethoxylated alcohols.

The preparation of glycosides containing alkoxy groups between the fatty residue and the  
15 saccharide portions of the glycoside molecule are described in U. S. Patent 3,219,656 to Boettner issued November 23, 1965. Alkyl polyglycosides are described in U. S. Patent 3,598,865 issued August 10, 1971 to Lew.

20 Glycosides containing ethylene glycol residues are described in U. S. Patent 3,737,426 issued June 5, 1973 to Throckmorton et al. The reader is also referred to Tenside Detergents; January/February 1973; New Biodegradable Surfactants Derived From Starch: Preparation and Properties; Throckmorton et al.  
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It has now been determined that the residual fatty alcohol leftover from preparing a glycoside can effectively be minimized through stripping out the excess alcohol and alkoxyating the remainder of the material  
30 therein. The reduction of lower glycoside content increases the cleaning ability of the desired products described herein. It has also been found that the alkoxyated glycosides having a long chain hydrophobic

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group are excellent surfactants. In particular, it has been found that the alkoxyated glycoside surfactants  
5 need not be as highly polymerized with regard to the saccharide due to the inclusion in the molecule of substantial amounts of lower alkylene oxide units.

Throughout the specification and claims percentages and ratios are by weight, temperatures are in  
10 degrees Celsius and pressures are in KPascals over ambient unless otherwise indicated. The references cited in this patent are to the extent applicable herein incorporated by reference.

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SUMMARY OF THE COMPOSITION OF THE INVENTION

The first aspect of the present invention describes  
5 a glycoside composition comprising:

(a) from about 50 parts to about 80 parts by weight of a glycoside of the formula  $R(OG)(EO)_y$  wherein R is from about 10 to about 20 carbon atoms, (OG) is a member selected from the group consisting of fructoside, glucoside, mannoside, galactoside, taloside, gulose, alloside, altroside, idoside, arabinoside, xyloside, lyxoside and riboside and mixtures thereof, EO is an ethylene oxide residue, and y is the average degree of ethylene oxide substitution on the glycoside;

(b) from about 8 parts to about 40 parts by weight of a glycoside of the formula  $R(OG)_x(EO)_y$  where R is from about 10 to about 20 carbon atoms, x is at least 2; (OG) is a member selected from the group consisting of fructoside, glucoside, mannoside, galactoside, taloside, gulose, alloside, altroside, idoside, arabinoside, xyloside, lyxoside and riboside and mixtures thereof, EO is an ethylene oxide residue; and y is the average degree of ethylene oxide substitution on the glycoside, and;

(c) from about 0 parts to about 12 parts by weight of a glycoside of the formula  $L(OG)_z(EO)_y$ , where L is from about 1 to about 4 carbon atoms, z is at least 1; (OG) is selected from the group consisting

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5 of fructoside, glucoside, mannoside, galactoside, taloside, guloside, alloside, altroside, idoside, arabinoside, xyloside, lyxoside and riboside and mixtures thereof, EO is an ethylene oxide residue, and y is the average degree of ethylene oxide substitution on the glycoside.

10 A second embodiment of the present invention is a glycoside composition comprising:

15 (a) from about 40 parts to about 90 parts of a glycoside of the formula  $R(OG)(AO)_y$  wherein R is from 10 to 20 carbon atoms, (OG) is a member selected from the group consisting of fructoside, glucoside, mannoside, galactoside, taloside, guloside, alloside, altroside, idoside, arabinoside, xyloside, lyxoside and riboside and mixtures thereof, AO is an alkylene oxide residue, and y is the average degree of alkylene oxide substitution on the glycoside;

25 (b) from about 5 parts to about 55 parts by weight of a glycoside of the formula  $R(OG)_x(AO)_y$  wherein x is at least 2, R contains from about 10 to about 20 carbon atoms, (OG) is a member selected from the group consisting of fructoside, glucoside, mannoside, galactoside, taloside, guloside, alloside, altroside, idoside, arabinoside, xyloside, lyxoside and riboside and mixtures thereof, AO is an alkylene oxide residue, and y is the average degree

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of alkylene oxide substitution on the glycoside;  
and,

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(c) from about 0.1 parts to about 9.5 parts by weight of a glycoside of the formula  $L(OG)_z(AO)_y$  where L is from about 1 to about 4 carbon atoms; z averages at least 2; (OG) is selected from the group consisting of fructoside, glucoside, mannoside, galactoside, taloside, gulose, allose, altrose, idose, arabinoside, xylose, lyxose and ribose and mixtures thereof, AO is an alkylene oxide residue and mixtures thereof, and y is the average degree of alkylene oxide substitution on the glycoside.

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A third embodiment of the present invention is a glycoside composition comprising:

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(a) from about 15 parts to about 100 parts by weight of a glycoside of the formula  $R(OG)(AO)_y$  wherein R is from about 12 to about 20 carbon atoms;

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(b) from about 10 parts to about 60 parts by weight of a glycoside of the formula  $R(OG)_x(AO)_y$  wherein R is from about 12 to about 20 carbon atoms and x is at least 2;

30 provided further (OG) is selected from the group consisting of fructoside, glucoside, mannoside, galactoside, taloside, gulose, allose, altrose, idose, arabinoside, xylose, lyxose and ribose and mixtures

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thereof; AO is selected from the group consisting of ethylene oxide and propylene oxide and mixtures thereof; y is at least 1 and the ratio of (a) to (b) is at least as great as 3:2.

A still further embodiment of the present invention is a glycoside composition comprising:

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(a) from about 10 parts to about 100 parts by weight of a glycoside of the formula  $R(OG)(EO)_y$  wherein R is from about 12 to about 20 carbon atoms;

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(b) from about 10 parts to about 60 parts by weight of a glycoside of the formula  $R(OG)_x(EO)_y$  wherein R is from about 12 to about 20 carbon atoms and x is at least 2;

20 provided further (OG) is selected from the group consisting of fructoside, glucoside, mannoside, galactoside, taloside, guloside, alloside, altroside, idoside, arabinoside, xyloside, lyxoside and riboside and mixtures thereof; EO is an ethylene oxide residue; y is at least 1  
25 and the ratio of (a) to (b) is greater than 1.

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### DETAILED DESCRIPTION OF THE INVENTION

It has been found in the present invention that a  
5 high percentage of a long chain monoglycoside which has  
been substituted with an alkylene oxide gives excellent  
detergency properties. It has further been found that  
the polyglycoside components of the present invention  
can be utilized having a lower DP than was previously  
10 known and also provide excellent detergency.

A further advantage of the present invention is in  
the discovery that if the short chain glycoside content is  
diminished that detergency will also be substantially  
improved. Lower glycoside as used herein means those  
15 materials having a short chain hydrophobic group on the  
molecule. Even though the lower glycosides can be  
alkoxylated in accordance with the present invention  
thereby increasing the water soluble nature of the lower  
glycoside this does not render that material an effective  
20 detergent.

The glycosides employed may be any of the types of  
materials as previously described in the Summary,  
however, it is most preferred that glucose (dextrose) be  
the backbone thereby giving a glucosyl structure to the  
25 glycoside.

A glycoside is typically defined as the reaction  
product of a saccharide and hydrophobic moiety through  
an acetal mechanism. While etherification of a hydroxyl  
on the saccharide can give a glycoside, the acetal  
30 mechanism is the preferred route to the glycoside.

The compositions of the present invention are best  
practiced by obtaining a long-chain glycoside e.g.,  
where R is from 10 to 20 carbon atoms, preferably 12 to

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20 carbon atoms and most preferably 12 to 18 carbon atoms in length. The value of R is also preferably an alkyl group, although alkenyl groups may also be employed. Similarly, the value of R may contain an aromatic group such as an alkylphenyl, phenylalkyl, alkylbenzyl or the like. The hydrophobic group (R) on the glycoside molecule, may also be substituted. Where substitution on the hydrophobic group is present, it is usually a hydroxyl group. However, it is generally desired that the hydrophobic group not be substituted.

The value of L as defined herein represents a lower hydrophobic group such as methyl, ethyl, propyl, isopropyl, sec-butyl or n-butyl group. The presence of the lower hydrophobic group in the molecule results from the process used to obtain the glycoside. That is, the starting materials for the glycoside are typically from a mixture of a lower alcohol and the saccharides as described in the Summary. Accordingly, the lower glycoside is first formed and then converted to the higher glycoside.

The saccharides are typically reacted as in the U. S. Patent 4,223,129 issued September 6, 1980 to Roth et al. Basically, the lower glycoside is an intermediate product from the reaction of the saccharide and a short chain alcohol. The higher hydrophobic values for R as previously described (fatty alcohol) are obtained by transesterification of the lower glycoside with a higher alcohol. The lower glycoside as described in the Summary may be effectively removed by minimizing the amount left in the reaction mixture e.g., pushing the conversion to the higher glycoside to completion. If

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large amounts of lower glycosides are present during alkoxylation, they compete with the desired glycoside for the alkoxy group. It has been observed that the short chain glycosides are more reactive with the alkylene oxides than the higher glycosides thus making the removal of the former highly desirable. It has not previously been recognized that the lower glycoside is detrimental to the detergency of the higher glycoside product. Thus reducing the lower glycoside content is desirable. It is further suggested that the lower glycoside may be minimized by stripping or by precipitation due to differential solubility of the lower and higher glycosides in various solvents.

After the higher glycoside containing the requisite amount of lower glycoside is obtained, it is possible to react the higher glycoside to increase the DP of the saccharide material. The DP may be increased by heating in the presence of acid catalysts. An advantage of the present invention is that it has been determined by preparing the end components as described herein that the DP of the alkoxyated glycoside need not be as high as believed required for a non-alkoxyated glycoside and yet be an effective detergent product. This is important as processing to increase the DP has the effect of darkening the product. A darkened product is of restricted value in formulations where light color is important. The value of  $x$  (DP) in the polyglycoside is typically from about 2.2 to about 3.5.

The alkylene oxide units which may be used in the present invention for addition to the glycoside are preferably those which add a degree of water solubility

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to the molecule. This, of course, may be determined experimentally by the amount that the water solubility of the glycoside is increased over that of the basic glycoside molecule. Practically speaking, the alkylene oxide units of which the present invention is mainly concerned are those derived from ethylene oxide or propylene oxide. It should also be mentioned that mixtures of ethylene oxide and propylene oxide are also within the scope of the present invention. Capping of the glycoside molecule through sequential reactions whereby ethylene or propylene oxide is added first, and then an amount of the remaining alkylene oxide is added to the molecule are also contemplated herein.

It is also desirable that the alkylene oxide when added to the glycoside molecule polymerize to form multiple alkylene oxide units from a single hydroxyl group on the saccharide portion of the glycoside molecule. It is believed that the number 2 hydroxyl on the saccharide molecule is most reactive under base conditions and thus a desired product to be formed herein is one in which the glycoside is substituted in the 2 position. It should also be noted that when adding propylene oxide to the glycoside that the potential exists to form either a primary or secondary hydroxyl group depending on the reaction. The secondary hydroxyl group is not particularly desired but is not noted to be harmful to the detergency of the alkoxyated glycoside so formed.

The alkylene oxide may be added to the glycoside molecule by either acid or base catalysis. As acid catalysis favors polymer growth of the alkylene oxide

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unit, side reactions may occur to form a polyalkylene oxide structure rather than to add the alkylene oxide to the glycoside molecule. The foregoing reaction can become particularly prevalent if small amounts of water are present in the reaction mixture which than favors the formation of the glycol. It is therefore desired that the water content be no more than about 5 percent by weight; preferably no more than 1 percent by weight of the reaction mixture. A preferred base for use in the present invention is an alkoxide-hydroxide such as those obtained from a mixture of the sodium or potassium hydroxide and methanol. The foregoing catalyst favors mono addition of the alkylene oxide to the free hydroxyls on the glycoside molecule.

The amount of the alkylene oxide added in the reaction is conveniently from about 1 mole to about 50 moles; preferably about 3 moles to about 20 moles by weight of the alkylene oxide per mole of the starting glycoside. The value of  $y$  which is a positive number indicates the degree of alkylene oxide adduction on the glycoside molecule. The alkylene oxide units may be block or randomly distributed. The average amount of alkylene oxide on the molecule is conveniently from about 1 to about 40; preferably from about 1 to about 30 moles per mole of glycoside.

While this invention suggests reacting a preformed long chain glycoside with an alkylene oxide, it is possible to alkoxyate a short chain glycoside and to then increase the hydrophobic chain length of the glycoside. Alternatively, the saccharide molecule may be reacted with the alkylene oxide and thereafter converted

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to the glycoside by reaction with a short chain or long chain alcohol. In the former case the short chain  
5 alkoxyated glycoside is then converted to the long chain alkoxyated glycoside.

It is believed that the amount of lower glycoside remaining in the product is detrimental to the overall effectiveness of the long-chain alkoxyated glycosides as  
10 a detergent. Therefore, it is desirable to minimize the glycoside content where the hydrophobic moiety (L), as previously described, is 4 or below. Thus the product is desired to be substantially free of lower glycosides. The mechanism for reducing the lower glycoside content  
15 has been previously discussed. It is also believed, that when the lower glycoside content is present in unrestricted amounts that the value of R in the long-chain glycoside must be increased. Where unrestricted amounts of lower glycosides are present increased  
20 amounts of long-chain alkoxyated glycosides (whether the mono or polyglycoside) should be present (or added) to compensate for the presence of the lower glycoside.

It is further desirable herein that the amount of alkoxyated higher glycoside, (higher monoglycoside plus  
25 the higher polyglycoside) be within a weight ratio to the lower glycoside (alkoxyated or not) of from about 40:1 to about 6:1; preferably at least 10 times the amount of the lower glycoside. It is also preferred that the higher alkoxyated monoglycoside (a) to the higher alkoxyated  
30 polyglycoside (b) should be greater than 1:1; especially from about 9:1 to about 3:2; preferably from about 8:1 to about 2:1.

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It is also desirable that the free fatty alcohol content in the present invention be less than about 2%;  
5 preferably less than 0.5% by weight as this material has been determined to interfere with detergency.

It is further desired that the alkylene oxide on either the long-chain monoglycoside or the long-chain polyglycoside contain at least one unit of repeating  
10 alkylene oxide units, e.g. polymerized with respect to the alkylene oxide. It is believed that through the polymerization of the alkylene oxide on the glycoside molecule that enhanced detergency will occur over a random distribution of the alkylene oxide around the  
15 hydroxyls on the glycoside molecule.

The reaction to add the alkylene oxide to the glycoside may be done in the presence of a solvent, typically an alcohol or an alkane. A suitable alkane is hexane, while the alcohol may be reactive or non-  
20 reactive to the alkylene oxide. A non-reactive alcohol is one such as t-butyl while a reactive alcohol is one such as any of the alcohols used to prepare the higher glycoside e.g., 10-20 carbons. If a reactive alcohol is used, it may be allowed to form the alkoxylate at from 0%  
25 to 90%; preferably 5% to 80% by weight of the total detergent product. The foregoing is particularly useful where the alkoxylate of the reactive alcohol is capable of functioning as a surfactant.

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EXAMPLE I

5 The following is a suggested exemplification of the present invention. A reaction vessel containing a stirring mechanism is obtained. 90 parts of dodecyl polyglycoside mixture obtained from dextrose is added to the reaction vessel. The alkylpolyglycoside mixture contains 1.2% moisture, 0.4% dodecyl fatty alcohol and an additional 10 parts of Neodol 23 alcohol from Shell. The Neodol 23 alcohol is approximately a 1:1 mixture of dodecyl and tridecyl alcohols. The DP of the polyglycoside is approximately 2.95.

15 The contents of the reaction flask are heated to about 140-150°C and 0.75 parts of potassium hydroxide dissolved in 1.7 parts of methanol is added to the reaction vessel.

20 The alkylene oxide utilized herein is propylene oxide and 12.7 parts is slowly added with the temperature maintained at from 125-130°C. It is observed that the viscosity of the reaction mixture is lowered as the propylene oxide is adducted to the alkylpolyglycoside.

25 The reaction mixture is then purified and tested for its detergency. The product is observed to clean better than the starting glycoside. Substantially similar results are observed when 1% by weight of butyl glycoside or its alkoxylates (DP 2.95) remain in the product following propoxylation.

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EXAMPLE II

5 A sealed reaction vessel of sufficient design to withstand 10,000 KPa pressure is evacuated and then charged with 307.5 parts of Product A which is 25.7% by weight dodecyl alcohol; 8.2% butyl glycoside; 66.1% dodecyl glucoside and 0.21% sodium methoxide. The glucosides are 1.4 DP.

10 Ethylene oxide is added to the reaction vessel to a pressure of 340 KPa. The reaction vessel is heated to 135°C and maintained between 135°C and 150°C until 161 parts of ethylene oxide is taken up. This first run (B) is divided into 2 parts. One part is further reacted (to  
15 give Product C) by introducing 1.2 parts of additional sodium methoxide, repressurizing as was previously discussed and further adding of ethylene oxide at 140-150°C until an additional 172 parts of ethylene oxide is consumed. Product B contains about 5 moles of  
20 ethylene oxide per mole of glucoside while Product C contains 10 moles of ethylene oxide per mole of glucosides.

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EXAMPLE III

5       The products of Example II are tested as shown  
below. The results show a product (B) made according  
to the invention to be superior in wetting ability to  
Product A the standard. Product C made according to  
the present invention is superior in foaming to Product  
A. Products B and C exhibit excellent cloud points  
10       when compared to Product A. The cleaning properties  
of Products B and C are observed to be superior to  
Product A in cleaning cotton/polyester and cotton fab-  
rics.

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TABLE I

<u>Produce Tested</u>	<u>Sample A (No EO)</u>	<u>Sample B (5 mole EO)</u>	<u>Sample C (10 mole EO)</u>
Draves (Seconds)	58	24	65
Ross Miles Foam Height 0 min.	15 mm	78 mm	87 mm
Ross Miles Foam Height 5 min.	15 mm	78 mm	87 mm
Surface Tension (Dynes/cm) .01%	32.4	30.9	31.6
Surface Tension (Dynes/cm) .10%	26.8	30.8	27.2
Cloud Point (1% Solution)	Cloudy at 22°C	Over 93°C	Over 93°C
Cloud Point (1% Solution in 10% NaCl)	----	87°C	74°C

What is Claimed is:

1. A glycoside composition comprising an alkoxyated long chain monoglycoside of the formula  $R(OG)(AO)_y$ , an alkoxyated long chain polyglycoside of the formula  $R(OG)_x(AO)_y$  and, optionally, an alkoxyated short chain glycoside of the formula  $L(OG)_z(AO)_y$  which may be a monoglycoside, a polyglycoside or a mixture thereof wherein R is a  $C_{10-20}$  hydrophobic group, L is a  $C_{1-4}$  hydrophobic group, G is a glycoside moiety, AO is an alkylene oxide selected from the group consisting of ethylene oxide, propylene oxide and mixtures thereof, y is at least 1, z is at least 1 and x is at least 2 and wherein said composition is further characterized as satisfying one or more of the following compositional requirements:

(a) AO is ethylene oxide and said composition comprises from 50 to 80 parts by weight of the ethoxylated long chain monoglycoside, from 8 to 40 parts by weight of the ethoxylated long chain polyglycoside, and from 0 to 12 parts by weight of the ethoxylated short chain glycoside; or

(b) z is at least 2 and said composition comprises from 40 to 90 parts by weight of the alkoxyated long chain monoglycoside, from 5 to 55 parts by weight of the alkoxyated long chain polyglycoside, and from 0.1 to 9.5 parts by weight of the alkoxyated short chain polyglycoside; or

(c) R is a  $C_{12-20}$  hydrophobic group and said composition comprises from 15 to 100 parts

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35 by weight of the alkoxylated long chain monoglycoside and from 10 to 60 parts by weight of the alkoxylated long chain polyglycoside, the weight ratio of the former to the latter being at least 3:2; or

40 (d) R is a C<sub>12-20</sub> hydrophobic group and AO is ethylene oxide and said composition comprises from 10 to 100 parts by weight of the ethoxylated long chain monoglycoside and from 10 to 60 parts by weight of the ethoxylated long chain polyglycoside, the weight ratio of the  
45 former to the latter being greater than 1:1.

2. The composition of Claim 1 wherein the glycosides are glucosides.

3. The composition of Claim 1 wherein R contains from 12 to 18 carbon atoms.

4. The composition of Claim 1 wherein R and L are alkyl groups.

5. The composition of Claim 1 wherein the weight ratio of the alkoxylated long chain monoglycoside to the alkoxylated long chain polyglycoside is from 9:1 to 3:2.

6. The composition of Claim 1 which is essentially free of unreacted fatty alcohol.

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7. The composition of Claim 1 wherein y is from 1 to 40.

8. The composition of Claim 1 wherein y is at least 2.

9. The composition of Claim 1 wherein x averages from 2.2 to 3.5.

10. The composition of Claim 1 wherein at least some alkoxylated short chain glycoside is present and wherein the weight ratio of the combined alkoxylated long chain monoglycoside and polyglycoside content to the alkoxylated short chain glycoside content is from 40:1 to 6:1.

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# INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/ 000376

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. <sup>4</sup> C07H 1/00, 15/00		
U.S. CL. 536/4.1, 18.3, 18.6		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
U.S.	536/4.1, 18.3, 18.6	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>8</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
A	US, A, 3,219,656 Published 23 November 1965, Boettner.	1-10
A	US, A, 3,958,865 Published 10 August 1971, Lew.	1-10
X	US, A, 3,640,998 Published 8 February 1972, Mansfield et al.	1-10
A	US, A, 3,737,426 Published 5 June 1973, Thockmorton et al.	1-10
A	US, A, 4,223,129 Published 16 September 1980, Roth et al.	1-10
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>3</sup>		Date of Mailing of this International Search Report <sup>3</sup>
18 April 1986		02 MAY 1986
International Searching Authority <sup>1</sup>		Signature of Authorized Officer <sup>20</sup>
ISA/US		Johnnie R. Brown

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A

US,A, 4,483,779 Published  
20 November 1984,  
Llenado et al.

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V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>10</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:

2. ☐ Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>11</sup>

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.